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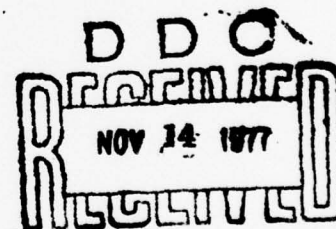
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A literature search was undertaken to collect information on cements which could be used in structural concrete and would cure at low temperatures. In the literature search, 18 types of cements or concretes manufactured by various firms were reviewed. Trade names are identified with their cement or concrete description, temperature range for curing, use experience and application, approximate cost (in 1976), and reference source or manufacturer. ←		

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PREFACE

This report was prepared by Robert Johnson, Research Civil Engineer, Foundations and Materials Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. It was funded by DA Project 4A762730AT42 *Design, Construction and Operations Technology for Cold Regions*, Task A3, *Facilities Technology/ Cold Regions*, Work Unit 008, *Placement of Construction Materials in Cold Regions*.

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CEMENTS FOR STRUCTURAL CONCRETE IN COLD REGIONS

INTRODUCTION

The recent pipeline construction activity in the State of Alaska has focused greater attention on the utilization of conventional construction engineering methods in permafrost areas. Due to the frailty of the tundra during the summer season, a major portion of the construction must be carried out during the winter. The problems related with frozen materials are compounded by extreme low temperatures. A major problem confronting design and construction by engineers and cement manufacturers is the curing of portland cement concrete. The problem is twofold: 1) preventing freezing of the concrete during curing to obtain design strengths, and 2) preventing thawing of the permafrost substrate by the cement heat of hydration release.

The standard methods of preventing freezing are to provide heated construction enclosures or use heated concrete materials. Extra equipment, labor and materials are needed to construct the enclosures and to heat the materials.

There are products on the market today which have potential for use in cold weather concreting. The purpose of this report is to provide a bibliography of available information on these products.

CEMENT VARIATIONS

Cements vary due to the raw materials used, the percentage composition of chemical compounds, and particle fineness. Some cements are designed with special properties for specific construction tasks. Such cements produced by different manufacturers may have widely different workability, strength and durability properties.

Fineness of the cement is an important variable that affects such paste properties as workability, durability, strength and curing time. Making the supposition that particle size distribution is the only factor that affects paste workability, Vivian (1966) states that when the mean particle size distribution decreases, the paste workability-water content relationship should approach a minimum. This means that a lower water cement ratio, which leads to an increased initial rate of compressive strengths gain, is attained with increased fineness of the cement particles. However, when the amount of very fine particles exceeds 15-20% of the cement by weight, the strength of the concrete declines.

HYDRAULIC CEMENTS

Hydraulic cements are those in which hydration is the principal reaction in concrete curing. Natural hydraulic cements are produced when a naturally occurring mixture of argillaceous and calcareous substances are calcinated at a temperature below that which sintering takes place. The most common argillaceous materials are clays, shales, and marls, and the most important calcareous material is limestone. Cements which are not based entirely on these two components may use three or more components to obtain a required control of composition. Taylor (1964) refers to the added components as "correcting" materials. Some of these correcting materials are iron oxide in various forms, bauxite or kaolin to make up the deficiencies in alumina content, and sand or sandstone to give sufficient silica.

A small amount of gypsum is also added to these cements to control the setting properties. The small percent of gypsum retards the hydration of the aluminate component of the cement and controls the tendency of the raw cement to flash set with the addition of water. Taylor (1964) reports that the setting rate and the compressive strength of Roman pozzolana mortars are favorably influenced by a limited addition of gypsum. A quantity of gypsum or calcium sulphate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), corresponding to 5-6% by weight of pozzolana, increases the compressive strength considerably, but with over 10% of gypsum, the mortar first cracks and ultimately becomes soft and incoherent when cured in water. Lea (1956) explains that when the pure cement compound tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) is mixed with water, the addition of gypsum will render the mass more plastic.

HIGH-ALUMINA CEMENTS

High-alumina cement is a mixture of pulverized fused limestone and bauxite (raw materials). Taylor (1969) indicates that this cement can be used at very low temperatures provided that there is adequate bulk and protection against frost action for the first 4 to 6 hours. Pendergrast (1972) warns against placing this type cement at ambient temperatures above 32.2°C (90°F) when considerable moisture or high relative humidity is present. He also warns of heat evolved during the first 24 hours of hydration, which will produce shrinkage cracks and reduced ultimate strength unless curing includes wetting during this initial period of time. Perhaps membrane curing would hold enough moisture to prevent the need of wetting. According to Stude (1969), high alumina cements do not show an initial evolution of heat, but after approximately two hours, the liberation of heat proceeds very rapidly. This is with the exception of those containing gypsum.

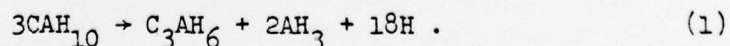
High alumina cements are white or grey in color. The white calcium aluminate cement is extra high in alumina with negligible amounts of iron oxide and silica; its composition is tricalcium penta-aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$). The grey high alumina cement is predominantly monocalcium aluminate ($\text{CaO}\cdot\text{Al}_2\text{O}_3$) as compared to the tricalcium aluminate composition of normal portland cement ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$). Maier et al. (1971) state that the predominantly monocalcium aluminate cement contains no free lime and none is produced upon hydration. Therefore, the addition of fly-ash or pozzolan creates only diluents and no additional cementitious reaction occurs.

From tests conducted at Point Barrow, Alaska, White (1952) found that a special cement manufactured from bauxite, without additives, had an unusual characteristic of setting quicker at a temperature of 45°C (113°F) than at 21°C (70°F). Robson (1962) indicates there is evidence that, in the temperature range between 1°C and 18°C (33.8° and 64.4°F), the setting-time is somewhat faster at about 10°C (50°F) than it is above or below that temperature. It is also observed that the maximum rate of heat evolution occurs around 10°C (50°F).

It is reported that, based on standard setting-time tests, the average setting times of high-alumina cements are longer than those of most portland cements, and that the Gillmore test tends to give longer setting times than the Vicat test. Once the initial set has been reached, the high alumina cement will gain strength at a very rapid rate. This is not the case with standard portland cements where the strength gain is very slow after the initial set, making the practical "working time" of portland cement longer than that of high alumina cement.

CONVERSION IN HIGH-ALUMINA CEMENT

Disregarding cost, Johnston (1975) states that the main reason that high-alumina cement has not been widely used in load-bearing applications is because of various examples of poor field performance through the years. The reason for the poor performance was not fully understood until the phenomenon of conversion and its associated significant drop in strength and increase in permeability were recognized. According to the booklet "Properties and Uses of Fondu Calcium Aluminate Cement" by the Lone Star Lafarge Company, the chemical reactions which take place during conversion are 1) the mono-calcium aluminate CA^* reacts with water, 2) the less stable hexagon hydrate $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ or CAH_{10} and alumina gel (AH_3) are formed initially, and 3) under the suitable conditions, the hexagonal CAH_{10} recrystallizes into AH_3 and forms the stable cubic C_3AH_6 with the evolution of water, as shown in



*customary abbreviations are: $\text{C}=\text{CaO}$, $\text{A}=\text{Al}_2\text{O}_3$, $\text{F}=\text{Fe}_2\text{O}_3$, $\text{S}=\text{SiO}_2$, $\text{H}=\text{H}_2\text{O}$

The above reaction depends on time, temperature, and the presence of water. The rate of the reaction increases with the simultaneous presence of moisture and temperature above 25°C (77°F), but proceeds at such a slow rate below the temperature of 25°C that it may be of little practical significance for cold weather concreting. Since the volume occupied by the hexagonal hydrates is greater than the volume occupied by the converted cubic hydrates, the concrete becomes more permeable and decreases in strength.

Newman (1960) reports that high alumina cement concrete that has been affected by hot moist conditions has a noticeable brown color and lower strength, which is related to the change in the nature of the hydration products. After prolonged curing the metastable compounds $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ and $2\text{Ca} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ produced at ordinary temperatures are converted into the cubic form of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. He indicates that the conversion is very slow in ordinary temperatures and probably never occurs in dry concrete. However, during setting and curing of high alumina cement, the large temperature rise inside massive concrete and the moist condition of the concrete at this stage produce ideal conditions for conversion.

To prevent appreciable conversion and produce a normal concrete, Robson (1962) suggests it is probably necessary to ensure that 1) the maximum temperature in the hardening concrete never exceeds about 59°C (122°F), 2) temperatures above 38°C (100°F) are reduced as quickly as possible, and 3) the concrete temperature is below 25°C (77°F) by the end of the first 24 hours.

A research team formed in February 1974 with staff from the Building Research Establishment (Great Britain) investigated the properties of high-alumina cement, collating and analyzing information for more than 400 high-alumina cement buildings. It reports that measurements of the degree of conversion of the concrete in existing buildings indicate that most concrete had reached a high level of conversion within a few years. Long-term laboratory studies showed that if the concrete is subjected to temperatures in excess of 25°C (77°F), which in its early life need only be for a few hours at any time during curing or subsequently, conversion becomes more rapid and a serious loss of strength occurs which may take some months to develop (Building Research Establishment 1975).

HIGH-MAGNESIA CEMENTS

The high magnesia cements are those which contain a large percentage of magnesia in the raw materials, for example dolomitic limestones. These materials are restricted by the ASTM to 5% total magnesia and to 4% by British standards. Amounts of magnesia in cements greater than these standards cause long-term volume instability in the cement concrete because of the presence of too much free magnesia (periclase).

According to Gaze and Smith (1973-1974), the cement clinker may contain magnesia in the glassy phase and crystalline compounds or free "hard-burned" crystalline MgO (periclase) during manufacturing. It is only in the latter state that it is capable of causing expansion by its hydration to $Mg(OH)_2$, which takes place slowly since the periclase is hard-burned. The reaction, accompanied by a volume increase of more than 100%, leads to possible disruption of the mortar or concrete long after it has hardened. The time involved for the expansion of specimens stored at ordinary temperatures has been observed at as little as 10 and as much as 40 years. However, final expansions were observed in high-magnesia cements held in continuous water storage at $50^{\circ}C$ ($122^{\circ}F$) within about one year. Further tests are in progress on the effect of different curing temperatures on the time to achieve maximum expansion. Table I provides a brief description of each cement or cement concrete listed which has magnesia in its compound composition.

PORTLAND TYPE III AND REGULATED-SET CEMENTS

Portland cement type III, high-early-strength, differs from type I mainly in the fineness of the ground cement, an increase in the compound composition of tricalcium silicate ($3CaO \cdot SiO_2$), and a decrease in dicalcium silicate ($2CaO \cdot SiO_2$). The tricalcium silicate hardens rapidly and is largely responsible for the initial set and early strength (PCA 1968).

The Portland Cement Association (PCA) holds a patent on regulated-set cement which contains a reduced amount of dicalcium silicate as compared to standard cement and no tricalcium aluminate. The tricalcium aluminate has been replaced by calcium fluoroaluminate, according to Houston and Hoff (1975) (it is also referred to as calcium alumina silicate by Pendergrast 1972). This cement has great potential for cold weather concreting because it will obtain its initial set at an ambient temperature of $-9.4^{\circ}C$ ($15^{\circ}F$).

Just as tricalcium aluminate imparts the initial strength to standard portland cements, calcium fluoroaluminate imparts the initial strength to the regulated-set cement. After the initial strength gain of about 1000 psi (6900 kPa) in approximately 1-1 1/2 hours from the calcium fluoroaluminate, no other strength gain occurs until the normal silicate hydration begins after about one day. Therefore, after the accelerated initial strength gain, the regulated-set cement should gain strength during curing similarly to standard portland cement types I and II.

In a cooperative test, CRREL and the New Hampshire Department of Public Works and Highways poured on experimental regulated-set cement slab in an unheated warehouse in New London, New Hampshire, to investigate curing time and strength relationships. The slab was poured in

January of 1976 at an ambient temperature of -8.9°C (16°F). Approximately one-half hour after placement, workmen could walk on the freshly poured slab without any visible adverse affects. The slab was dry with no surface bleeding of mix water. Further information on regulated-set cement is contained in Houston and Hoff (1975).

GYPSUM PLASTER AND GYPSUM CEMENT

Gypsum plaster and cement are manufactured from natural deposits of gypsum. Finely ground gypsum is heated to 150°C (302°F) in open vessels to obtain a hemihydrate mixed with unchanged gypsum known as plaster of Paris. This product has a very rapid setting rate due to the presence of unchanged gypsum. To retard the setting of plaster of Paris, 0.1% by weight of a protein called keratin is added. This retarder usually delays the reaction to a moderate set time of 1 or 2 hours. Further calcination at higher temperatures (190 - 200°C) produces an anhydrous gypsum plaster, and when the calcination is carried to 600°C , in the presence of an accelerator, the product formed is known as Keen's or Parisian cement, which has a moderate setting rate. Calcining gypsum at 1100 - 1200°C produces a very slow setting product known as Estrich Gips, a German flooring plaster (Lea 1956). Taylor (1964) reports that gypsum in the form of calcium sulphate is universally added to portland cement clinker to retard initial chemical reaction which would otherwise produce flash set.

White (1952) conducted tests on a gypsum cement with a setting time of 60 minutes. The cement samples set at -9.4°C (15°F) and were found to be unfrozen at the time of final set. Included in his work is a table of initial and final setting times which shows a water/cement ratio of 0.44 with 4% calcium chloride in the mixing water. This sample had an initial set at -9.4°C (15°F) in 1 hour, 56 minutes and a final set in 2 hours, 19 minutes.

It was noted that the water used in the tests with gypsum cement was obtained from lakes scattered throughout the Naval Petroleum Reserve No. 4 located north of the Brooks Range in Alaska.

HEAT OF HYDRATION

The thermal properties of curing concrete are important when the concrete is to be poured for foundations on frozen or permafrost soil. The maximum concrete temperature during the liberation of the heat of hydration is an important parameter with high ice content soils, since melting will cause significant alignment and loading problems.

Rapid curing concretes are usually associated with a high rate of liberation of the heat of hydration. There has to be a trade-off between slow liberation, which does not produce melting and yet does not allow the concrete to freeze before gaining strength, and high liberation which gives heat and prevents freezing but could cause melting of frozen soil.

CEMENT BLENDS

Stude (1969) found that by adding fly-ash to high-alumina cement mixes the heat evolved at a slower rate, but that there was a strength decrease when compared with no addition of fly-ash. Kennedy (1957), investigated pozzolan and other materials for their use as partial replacements for portland cements and found that the materials appear to rank in the following order in their ability to reduce the early evolution of heat: slag and obsidian, pumicite and calcined shale, fly-ash, tuff and calcined diatomite, natural cement, and uncalcined diatomite.

Variations in initial set times of cements can be controlled by varying the percentages of different cement mixtures. White (1952) conducted tests with mixtures of gypsum and other cements and found that it was possible to design such cement mixtures for a given set time period. Readers may be interested in the results of blending lumnite (high-alumina cement) and regulated-set cements as reported by Bussone et al. (1972), who also tested blends of gypsum cement, various normal portland cements, high-alumina cement and regulated-set cement, and the addition of additives such as fly-ash, accelerators and retarders.

NONHYDRAULIC CEMENTS

Some cement producers may refer to nonhydraulic cements as those for which hydration is not the principal reaction. Such cements require an activator solution, which is referred to as a chemical solution other than water, to perform the cementation process. However, these cements are aqueous materials rather than synthetic resins (plastics). Temperatures below 0°C (32°F) will freeze aqueous materials like portland cement concrete, water emulsion glues, latex paints, asphalt emulsion, etc. (Sayward 1974). However, these activator solutions may possess a lower freezing point than that of ordinary water. There are such nonhydraulic concrete cements marketed which use a dry aggregate mix in conjunction with an activator solution to start the chemical reaction. See Table I for various cement producers.

CONCLUSION

During recent years, the discovery of oil near Prudhoe Bay, Alaska, has warranted the need for determining feasible cold weather construction engineering methods as well as seeking adequate engineering materials to utilize under such conditions. This report has reviewed various types of cements or cement concretes which possess curing properties that may be of value in cold environments or under low temperature conditions.

The low ambient temperature conditions also affect the rate at which the heat is liberated, implying an effect on the rate of curing of many concrete cements. As mentioned previously, it was found that as the ambient temperature was lowered from 21.1°C (70°F) to 4.4°C (40°F), the initial and final sets of a curing cement concrete test were obtained in less time.

Conventional use of cold weather concrete construction practices may be minimized or in some instances be replaced by new practices or materials as described in this report. However, cold weather concreting still remains a major economic and energy consumption problem, and overcoming the necessity of affording protection to ensure proper curing remains a major task for the future.

There is a need for research on the properties of curing concrete under cold or low ambient temperature conditions. The rate of heat evolved by the exothermic reaction of curing is of particular concern when cement concrete mixes must be placed on or near frozen ground where the heat evolved will cause melting. Information gained by research seeking to determine the maximum rates of heat evolved, the times when these maxima occur after mixing of a neat-cement mix, and the setting times of different mixes under low temperature ranges should prove valuable in the selection of cement or cement concrete for specific cold, frozen, or low temperature conditions. This information is usually not available from the various concrete cement manufactures.

RECOMMENDATIONS

Based upon the search for information compiled for this report, it is recommended that the following tasks be undertaken in order to obtain cold environment setting and curing data on the available concrete cements.

1. Synthesis of experience. In order to develop sufficient information on cement concrete setting and curing problems, various cement

manufacturers, agencies, and organizations interested or involved in cold weather concreting construction should be located, contacted, and a compilation of their interests and experiences made, including such information as field construction problems and cost effectiveness.

2. Laboratory testing. Cement or cement concrete manufacturers usually do not supply information on the effects of different low ambient temperatures (0°C or 32°F and below) on the setting and curing properties of their products. Various manufacturers should be contacted for obtaining representative samples of their products to laboratory test for setting and curing properties at low ambient temperatures. A detailed documentation should be made of the results of each sample tested, including an analysis of the advantages and disadvantages for cold weather setting and curing. Further testing on gypsum cements should be conducted to identify additional beneficial characteristics for their utilization in cold environments.

3. Field evaluation. A concrete test slab of sufficient size and configuration should be constructed to produce an adequate number of samples for validation of the laboratory tests. Construction of the test slab should take place in a field environment where the ambient temperature is below freezing (0°C or 32°F). A suitable location would be in Hanover, New Hampshire, or a similar environment during the winter months when low temperatures prevail. This would allow an in-depth evaluation of construction procedures and materials.

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TABLE I. PROPERTIES OF VARIOUS CEMENTS OR CONCRETES.

TYPE CEMENT OR CONCRETE	DESCRIPTION	TEMP. RANGE FOR CURING	EXPERIENCE AND USE	APPROX. COST (SPRING 1976)	REFERENCE OR MANUFACTURER
SET-45 CONCRETE	MAGNESIUM PHOSPHATE	32°F SET 60 MIN 40°F SET 8 MIN	PATCHING AND REPAIR	\$17.50/50# bg. or 8.55/50# bg. bulk	SET PRODUCTS TECH. DATA
REPUBLIC STEEL'S HIGH STRENGTH QUICK SETTING CONCRETE	POWDERED MAGNESIA & AN ACTIVATOR SOLUTION	20 MIN WORKING TIME AT 40°-50°F, AT 72°F SET IN 5-7 MIN	PATCHING AND REPAIR		REPUBLIC STEEL TECH DATA
DAREX 240 CONCRETE*	MAGNESIA & A LIQUID PHOSPHATE	30°F SET IN 1-1/4 HR 90°F SET IN 4-6 MIN	PATCHING AND REPAIR	\$22.00 per unit (50# bg binder/ aggregate & 1 gal. activator)	W.R.GRASE & CO.
BOSTIK 276* QUICK SET HIGHWAY CEMENT*	MAGNESIUM OXIDE & AMMONIUM PHOSPHATE LIQUID ACTIVATOR	30°F SET IN 170 MIN AT 90°F SET IN 5 MIN	PATCHING AND REPAIR	13.96-12.60/45#bg UPCO TECH DATA	
MEND-CON*		40°-90°F WORKING TIME 5-7 MIN	REPAIRING AND ANCHORING	\$118.25-\$110.25/ 105# Pre-act- ivated granular	NATIONAL CHEMSEARCH BUL. PC-13(8-75)
FASTCRETE*	MAGNESIA & LIQUID PHOSPHATE		PATCHING & REPAIR	\$20.65/61.5# UNIT	STEELCOTE MFG. CO.
ARMASET*	CALCINED MAGNESIA & AMMONIUM PHOS- PHATE SOLUTION	30°F SET IN 170 MIN AT 90°F SET IN 5 MIN	PATCHING & REPAIR		ACME HIGH PRODUCTS CORP.
DURACAL CEMENT	GYPSUM & PORT- LAND CEMENT BLEND PLUS IMPROVEMENTS TO EACH	32°F + AND ABOVE	REPAIRING ABOVE GRADE	\$125.00/TON	UNITED STATES GYPSUM TECH DATA
HALLIBURTON PERMAFROST CEMENT	GYPSUM & PORTLAND CEMENT BLEND	DESIGNED FOR 15° to 80°F (salt added) AT 20°F SET IN 12 to 24 HOURS	CEMENTING SURFACE CASING PIPE		HALLIBURTON TECH DATA SHEET C-199 JFT 10/1971

TABLE I. PROPERTIES OF VARIOUS CEMENTS OR CONCRETES (CONTINUED)

TYPE CEMENT OR CONCRETE	DESCRIPTION	TEMP. RANGE FOR CURING	EXPERIENCE AND USE	APPROX. COST (SPRING 1976)	REFERENCE OR MFG.
STRUCTO-CAL CEMENT	GYPSUM CEMENT	32°F + AND ABOVE	STRUCTURAL GROUTING	\$106.00/TON or \$125.00/TON (NEAT)	UNITED STATES GYPSUM BUL. NO. TAC -156
FIVE STAR HIGHWAY PATCH	PORTLAND CEMENT & SPHERES OF CARBON		PATCHING		FHWA-RD-74-55 ⁺
HYDRO-STONE SUPER X	ULTIMATE STRENGTH GYPSUM CEMENT	32°F + AND ABOVE	PATCHING & REPAIRS	\$104.00/TON	UNITED STATES GYPSUM TECH DATA (IGL-173)
1) LUMNITE 2) REFCON	CALCIUM ALUMINATE CEMENTS	ABOVE 32°F FOR FOR FIRST 24 HOURS	MANY PROJECTS IN FREEZING TEMP.	LUM-\$8.41/70#bg REF-\$9.54/70#bg	UNIVERSAL ATLAS CEMENT
FONDU	CALCIUM ALUMINATE CEMENT	ABOVE 32°F FOR FIRST FEW HOURS	UTILIZED IN COLD STORAGE PLANTS	4 X PORTLAND	LONE STAR LAFARGE CO
UNITED STATES GYPSUM VERY HIGH EARLY CEMENT	MODIFIED PORTLAND CEMENT	--	--	--	UNITED STATES GYPSUM (IN EXPERIMENTAL STAGES) PER-1976
REGULATED-SET	CALCIUM FLUOROALUMINATE	15°F AND ABOVE	**	+	HUSTON & HOFF (1975)
EXIDE MARI-CRETE	ACCELERATED (NO CALCIUM CHLORIDE)	40°F SETS IN 24 HRS 80°F SETS IN 6 MIN	CONCRETE REPAIRS ABOVE AND UNDER WATER		EXIDE MARI-CRETE BUL A-22
SECAR 250	CALCIUM ALUMINATE (EXTRA HIGH-ALUMINA)				CONCRETE TECHNOLOGY BY TAYLOR (1969)
SONOPATCH	MODIFIED PORTLAND CEMENT		CONCRETE REPAIRING	50#bg at \$0.16/#	SONNEBORD-CONTECH FORM NO. SC-230 15M6/75MF

⁺ Generally a little less than 2 x portland cement

* Republic Steel's licensee

+ Report Number FHWA-RD-74-55 (Federal Highway Administration Office of Research & Development, Washington, DC, 20590)

**See Portland Type III and Regulated-set Cements of this report.